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Liquid azide salts and their reactions with common oxidizers IRFNA and N$_2$O$_4$ (PREPRINT)

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Abstract. Several imidazolium-based ionic liquid azides with saturated and

unsaturated side chains were prepared and their physical and structural properties were

investigated. The reactivity of these new as well as some previously reported ionic liquid

azides with the strong oxidizers, N$_2$O$_4$ and inhibited, red-fuming-nitric acid (IRFNA),

were studied.

Introduction.

Ethylammonium nitrate is commonly regarded as the first reported room-temperature

ionic liquid (IL),[1] and was discovered just after two closely related compounds,

hydroxyethylammonium nitrate[2] and hydrazinium azide.[3] With melting points of 52-55°C

and 75°C, respectively,   these salts still qualify as ILs according to the common

definition: a salt with a melting point at or below 100°C. It is interesting to note that

these debut materials are not only ILs but are also energetic ILs, and have been used in

both explosive and propellant applications.[4-6] A propellant containing hydrazinium azide was test-fired and spontaneous ignition was achieved upon contact with inhibited, red-fuming nitric acid (IRFNA).[7] This is commonly referred to as hypergolic ignition and is very desirable for bipropellant applications due to its relative engineering simplicity and reliability.[8] Consequently, we became interested in the reactivity of recently described IL azides[9] with commonly used oxidizers such as IRFNA and N_2O_4. The latter was of particular interest because it is known that the azide anion reacts completely with N_2O_4 to yield only nitrates and the lightweight gases N_2, N_2O (eq. 1).

$$N_2O_4 + N_3^- \longrightarrow NO_3^- + N_2 + N_2O \qquad (1)$$
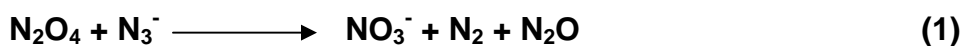
This reaction is thought to proceed through an unstable intermediate, NON_3, which has been the subject of multiple investigations.[10-12] If the N_3^-/N_2O_4 reaction provides enough heat to ignite a salt with a heterocyclic cation and an azide anion, these materials could be candidates as replacements for hydrazine in bipropellant applications.

The priority placed on finding a suitable replacement for the fuel component in bipropellant applications can be illustrated with the N_2H_4/N_2O_4 system. The dangers and operational costs associated with other methylated hydrazine fuels and nitrogen containing oxidizers are similar.

Although NO_2 and N_2O_4 are acute toxins, neither is listed by the IARC (International Agency for Research on Cancer), NTP (National Toxicology Program) or OSHA (Occupational Safety and Health Administration) as a carcinogen or potential carcinogen, as is hydrazine. The working concentrations permitted for NO_x (3 ppm) are

substantially higher than those for hydrazine (0.01 ppm). In addition nitrogen oxides

can be detected by their odor at levels considerably below the danger limits. In contrast,

hydrazine cannot be smelled until levels are nearly 400 times the recommended safe

concentrations. Hydrazine toxicity and containment are further exacerbated by its high

vapor pressure (13.87 kPa at 20°C). Therefore, replacing hydrazines with an IL which

generally possesses very low volatility, and therefore virtually no vapor toxicity, would

be extremely beneficial.

In addition to the currently reported imidazolium compounds which were chosen to

improve thermal stability, some previously reported amino triazolium azides[9] were

screened for hypergolicity with N_2O_4 and IRFNA. The synthesis and structural and

physical properties of some novel imidazolium azides with a variety of energetic, and

perhaps innately reactive, unsaturated sidechains are discussed. In one instance the

crystalline product of reaction with N_2O_4 was recovered. Its precise composition was

determined from an X-ray single crystal investigation.

Experimental Section.

Caution! None of the prepared azides showed particular sensitivity toward friction

(scratching with a metal spatula) or impact (hitting with a hammer), and no accidents or

mishaps occurred during work with these materials. However, the use of appropriate

safety precautions (safety shields, face shields, leather gloves, and protective clothing

such as heavy leather welding suits and ear plugs) are mandatory for work with any

*energetic materials, especially when working on a larger scale. **Ignoring safety***

precautions can lead to serious injuries!

All starting materials were purchased from Aldrich Chemical Company, Inc. and their purities were checked by ^{1}H and ^{13}C NMR prior to use. Acetonitrile (99.93+% HPLC grade), methanol (99.93% A.C.S. HPLC grade), diethyl ether (anhydrous, 99+%, A.C.S. Reagent) and the azide exchange resin (azide on Amberlite® IRA-400, 16-50 mesh ~3.8mmol N_3/g) were used as received. The substituted imidazolium halides[13] and the substituted triazolium azides[9] were prepared according to literature procedures. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting-point capillaries or 5mm glass NMR tubes were used as sample containers. IR spectra were recorded on a Mattson Galaxy FTIR spectrometer using a glass, gas IR cell equipped with CsI windows. NMR spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield[TM] spectrometer at room temperature with samples as neat liquids or dissolved in DMSO-d_6 using 5mm NMR tubes. The ^{1}H and ^{13}C spectra were referenced to external samples of neat TMS; ^{14}N spectra were referenced to external samples of neat nitromethane. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box. Viscosities were measured using a Brookfield RVDV-II+Pro viscometer equipped with a CPE-40 cone spindle at 10 RPM. The instrument was connected to a Brookfield TC-502 temperature controller set at 25°C.

General procedure for preparation of imidazolium salts (1-7). To a 100 mL Schlenk flask equipped with a Teflon[©] stir bar and purged with nitrogen the 1-R-3-methyl-imidazolium bromides were added and dissolved in ca. 30 mL of acetonitrile. A molar excess (up to 10 times) of azide exchange resin (3.8mmol N_3/g) was added to the stirred solution and stirring was continued for ~16h. The insoluble polymeric reagent was removed by filtration and the solvent was removed in a dynamic vacuum leaving behind the corresponding IL azides.

1-butyl-3-methyl-imidazolium azide (1). 1.37 g (6.24 mmol) 1-butyl-3-methyl-imidazolium bromide and 8.21 g (31.20 mmol N_3^-) of azide exchange resin were reacted. Amber liquid, yield 95%; melting point (peak): +36°C; decomp. onset +222°C. Raman (375mW, 25°C, cm^{-1}) $\nu = 3149(5), 3076(8), 2955(47), 2940(44), 2913(38), 2873(33),$ 2830(8), 2736(4), 1566(5), 1446(12), 1416(20), 1385(12), 1319(41), 1244(8), 1210(2), 1172(1), 1116(6), 1055(4), 1021(17), 975(0+), 950(0+), 906(2), 883(4), 827(4), 810(3), 734(0+), 699(3), 658(2), 623(4), 600(6), 500(1), 416(3), 326(4), 85(100); δ_{1H} (neat liquid) 8.83 (1H, s), 7.39 (1H, s), 7.29 (1H, s), 3.69 (2H, t, CH_2CH$_2$CH$_2$CH$_3$, J_{Hz} 6.5), 3.43 (3H, s, CH_3), 1.15 (2H, quintet, CH$_2$CH_2CH$_2$CH$_3$, J_{Hz} 6.9) 0.54 (2H, sextet, CH$_2$CH$_2$CH_2CH$_3$, J_{Hz} 7.2), 0.12 (3H, t, CH$_2$CH$_2$CH$_2$CH_3, J_{Hz} 7.3); δ_{13C} (neat liquid) 137.6, 123.8, 122.6, 49.1, 35.4, 32.0, 19.2, 13.0; δ_{14N} (neat liquid ($\Delta_{1/2}$, Hz)) -132 (25), -194 (145), -209 (140), -280 (85).

1-hydroxyethyl-3-methyl-imidazolium azide (2). 0.33 g (1.73 mmol) 1-hydroxyethyl-3-methyl-imidazolium bromide and 0.68g (2.58mmol N_3^-) of azide exchange resin were reacted. Clear liquid, yield 95%; melting point (peak): +36°C; decomp. onset +214°C. Raman (400mW, 25°C, cm^{-1}) $\nu = 3160(7), 3098(8), 2957(44),$

2886(13), 2834(7), 1565(4), 1452(7), 1417(19), 1386(8), 1334(21), 1247(3), 1196(1), 1075(4), 1022(16), 946(2), 874(4), 703(3), 652(1), 602(7), 495(4), 417(3), 331(2), 279(2), 85(100); δ_{1H} (DMSO-d_6) 9.13 (1H, s), 7.74 (1H, t, J_{Hz} 1.7), 7.71 (1H, t, J_{Hz} 1.7), 5.30 (1H, t, CH$_2$CH$_2$O*H*, J_{Hz} 5.0), 4.21 (2H, t, C*H$_2$*CH$_2$OH, J_{Hz} 4.8), 3.87 (3H, s, C*H$_3$*), 3.71 (2H, q, CH$_2$C*H$_2$*OH, J_{Hz} 4.9); δ_{13C} (DMSO-d_6) 137.3, 123.8, 123.1, 59.7, 52.0, 36.1; δ_{14N} (DMSO-d_6 ($\Delta_{1/2}$, Hz)) -131 (25), -210 (1300), -277 (145).

1-allyl-3-methyl-imidazolium azide (3). 0.88 g (4.36 mmol) 1-allyl-3-methyl-imidazolium bromide and 13.24 g (50.31 mmol N_3^-) of azide exchange resin were reacted. Dark amber liquid, Yield 72%; melting point (peak): +19°C; decomp. onset +150°C. Raman (500mW, 25°C, cm^{-1}) ν = 3153(4), 3082(9), 3019(23), 2981(18), 2951(29), 2826(3), 2801(2), 1645(15), 1565(3), 1472(5), 1412(15), 1384(5), 1318(34), 1293(7), 1244(7), 1173(0+), 1107(2), 1021(12), 947(4), 918(1), 756(5), 676(3), 624(4), 569(3), 501(2), 459(2), 397(1), 318(0+), 103(80), 84(100); δ_{1H} (DMSO-d_6) 9.26 (1H, s), 7.79 (1H, t, J_{Hz} 1.6), 7.78 (1H, t, J_{Hz} 1.7), 6.05-5.98 (1H, m, CH$_2$C*H*CH$_2$), 5.31-5.26 (2H, m, C*H$_2$*CHCH$_2$), 4.88 (2H, d, CH$_2$CHC*H$_2$*, J_{Hz} 6.0), 3.89(3H, s, CH$_3$); δ_{13C} (DMSO-d_6) 137.2, 132.2, 124.2, 122.8, 120.6, 51.2, 36.0; δ_{14N} (DMSO-d_6 ($\Delta_{1/2}$, Hz)) -132 (130), -205 (270), -277 (280).

1-(3-butenyl)-3-methyl-imidazolium azide (4). 0.70 g (3.23 mmol) 1-(3-butenyl)-3-methyl-imidazolium bromide and 9.05 g (34.39 mmol N_3^-) of azide exchange resin were reacted. Dark amber liquid, Yield 83%; melting point (peak): +45°C; decomp. onset +188°C. Raman (100mW, 25°C, cm^{-1}) ν = 3075(15), 3004(38), 2953(67), 2912(32), 1641(53), 1561(6), 1525(13), 1418(40), 1383(11), 1318(100), 1294(8), 1244(20), 1109(1), 1021(33), 843(5), 600(13), 492(0+), 123(47); δ_{1H} (DMSO-d_6) 9.13 (1H, s), 7.76

(1H, t, J_{Hz} 1.7), 7.68 (1H, t, J_{Hz} 1.7), 5.77-5.70 (1H, m CH$_2$CH$_2$C*H*CH$_2$), 5.05-5.00 (2H, m, CH$_2$C*H$_2$*CHCH$_2$), 4.25 (2H, t, J_{Hz} 6.8, C*H$_2$*CH$_2$CHCH$_2$), 3.84 (3H, s, CH$_3$), 2.55 (2H, d, J_{Hz} 6.8, CH$_2$CH$_2$CHC*H$_2$*); δ_{13C} (DMSO-*d$_6$*) 137.0, 134.0, 123.9, 122.8, 118.9, 48.4, 36.1, 34.0; δ_{14N} (DMSO-*d$_6$* ($\Delta_{1/2}$, Hz)) -133 (40), -199 (160), -209 (168), -284 (159).

1-(2-butynyl)-3-methyl-imidazolium azide (5). 1.15 g (5.35 mmol) 1-(2-butynyl)-3-methyl-imidazolium bromide and 14.07 g (53.47 mmol N$_3^-$) of azide exchange resin were reacted. Solid, Yield 65% (after recrystallization from methanol solution layered with diethyl ether); melting point (peak): +66°C; decomp. onset +115°C. Raman (500mW, 25°C, cm^{-1}) ν = 3098(7), 3074(7), 3015(15), 2959(30), 2917(51), 2741(4), 2324(6), 2248(36), 1569(5), 1459(9), 1425(13), 1408(24), 1381(21), 1329(21), 1322(49), 1267(1), 1243(11), 1174(5), 1106(7), 1088(6), 1020(20), 946(3), 883(4), 793(4), 748(9), 641(10), 629(9), 449(10), 403(12), 367(23), 322(13), 270(11), 196(21), 111(100), 84(83); δ_{1H} (methanol-*d$_4$*) 9.11 (1H, s), 7.71 (1H, d, J_{Hz} 2.0), 7.64 (1H, d, J_{Hz} 2.0), 5.10 (2H, q, J_{Hz} 2.5, C*H$_2$*CCCH$_3$), 3.99 (3H, s, CH$_3$), 1.94 (3H, t, J_{Hz} 2.4, CH$_2$CCC*H$_3$*); δ_{13C} (methanol-*d$_4$*) 136.2, 123.8, 121.9, 85.1, 69.5, 39.1, 35.2, 1.8; δ_{14N} (methanol-*d$_4$* ($\Delta_{1/2}$, Hz)) -133 (60), -201 (116), -208 (120), -283 (186).

1-(2-pentynyl)-3-methyl-imidazolium azide (6). 1.40 g (6.11 mmol) 1-(2-pentynyl)-3-methyl-imidazolium bromide and 3.21 g (12.20 mmol N$_3^-$) of azide exchange resin were reacted. Dark amber liquid, Yield 90%; melting point (peak): +19°C; decomp. onset +107°C. Raman (500mW, 25°C, cm^{-1}) ν = 3155(7), 3075(10), 2936(81), 2848(19), 2734(4), 2294(11), 2241(51), 1641(1), 1569(7), 1414(32), 1385(18), 1322(39), 1244(6), 1167(3), 1144(1), 1104(7), 1063(13), 1020(33), 961(11), 880(1), 756(7), 660(5), 636(6), 614(14), 512(4), 431(5), 401(10), 354(4), 271(12), 94(100); δ_{1H} (DMSO-*d$_6$*) 9.30 (1H, s),

7.80 (1H, s), 7.78 (1H, s), 5.18 (2H, s CH_2CCCH_2CH$_3$), 3.89 (3H, s, CH$_3$), 2.29-2.24 (2H, m, CH$_2$CCCH_2CH$_3$) 1.07 (3H, t, J_{Hz} 7.5, CH$_2$CCCH$_2$CH_3); δ_{13C} (DMSO-d_6) 136.9, 124.4, 122.5, 90.2, 72.2, 39.3, 36.3, 13.7, 12.1; δ_{14N} (DMSO-d_6 ($\Delta_{1/2}$, Hz)) -131 (67), -207 (670), -276 (165).

1-propargyl-3-methyl-imidazolium azide (7). 0.83 g (4.13 mmol) 1-propargyl-3-methyl-imidazolium bromide and 15.73 g (59.77 mmol N$_3^-$) of azide exchange resin were reacted. Upon addition of the exchange resin the solution turned dark brown. No unambiguous product was recovered.

In a modification to the general procedure, 0.38 g (1.89 mmol) of 1-propargyl-3-methyl-imidazolium bromide was added to a Schlenk flask and dissolved in ca. 30 mL of acetonitrile at +60°C. After all of the material was dissolved, the solution was cooled in an ice bath for 30 min before adding 0.57 g (2.17 mmol N$_3^-$) azide exchange resin. The solution was kept at 0 °C but after a short period of time the solution turned dark brown. Cold filtration again gave no isolable product.

1-methyl-1,2,4-triazolium nitrate (8). To a 25 mL glass reaction vessel equipped with a Kontes Teflon$^©$ valve, ca. 3 mL of N$_2$O$_4$ were condensed at -196°C. The valve was opened under a flow of dry nitrogen. A few mg of 1-methyl-4-amino-1,2,4-triazolium azide were added to the frozen N$_2$O$_4$ at -196°C. The mixture was allowed to warm to ambient temperature in the open reaction vessel with dry nitrogen purge. After ambient conditions were attained, the valve was closed and all volatiles were removed in a dynamic vacuum leaving behind a crystalline white solid. Melting point (decomp.): +241°C; Raman (500mW, 25°C, cm^{-1}) ν = 3127(13), 3036(18), 3022(20), 2963(24), 2878(4), 2805(6), 1647(2), 1564(7), 1472(10), 1443(11), 1419(11), 1403(7), 1365(31),

1264(7), 1245(7), 1159(4), 1120(19), 1079(5), 1040(100), 991(14), 928(12), 723(10),

715(7), 683(20), 674(24), 642(1), 375(5), 269(10), 148(31), 125(68), 102(67), 95(78),

85(85); δ_{1H} (MeOH-d_4) 9.66 (1H s), 8.78 (1H, s), 4.13 (3H, s, CH$_3$); δ_{13C} (MeOH-d_4)

145.6, 143.6, 38.7; δ_{14N} (DMSO-d_6 ($\Delta_{1/2}$, Hz)) -11 (18), -165 (215), -194 (238).

X-ray Analyses. The single-crystal X-ray diffraction data were collected on a Bruker

3-circle-platform diffractometer equipped with a SMART detector with the χ-axis fixed

at 54.74° and using MoK$_\alpha$ radiation (λ = 0.71073 Å) from a fine-focus tube. The

diffractometer was equipped with a KryoFlex apparatus for low temperatures using

controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon

Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil.

Cell constants were determined from 90 ten-second frames and a complete hemisphere of

data was scanned on omega (0.3°) at ten-seconds per frame and a resolution of 512 x 512

pixels using the SMART software.[14, 15] A total of 2400 frames were collected in four sets

and final sets of 50 frames, identical to the configuration of the first 50 frames, were also

collected to determine any crystal decay. The frames were then processed using the

SAINT software[16, 17] to give the hkl file corrected for Lp/decay. The absorption

correction was performed using the SADABS[18] program. The structures were solved by

the direct method using the SHELX-90[19] program and refined by the least-squares

method on F^2, SHELXL-97[20] incorporated in SHELXTL Suite 5.10.[21, 22] All non-

hydrogen atoms were refined anisotropically. For the anisotropic displacement

parameters, the U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

The hydrogen atoms were located either from difference electron density maps or

generated at calculated positions.

Results and Discussion

Syntheses. The different azide salts (**1-6**, Scheme 1) were readily prepared using an azide-exchange resin as previously described.[9] All salts are soluble in polar solvents such as acetonitrile, methanol, and water but are insoluble in diethyl ether, hexane, dichloromethane, and ethyl acetate. All salts were characterized by ^{1}H, ^{13}C and ^{14}N NMR, Raman spectroscopy, and DSC analysis. Viscosities were measured for liquid samples. The crystal structures of **5** and **8** were also determined.

All azides were easily identified by their characteristic symmetric-stretch vibration, ν_s N_3^-. It is the most intense band in the spectra (except for lattice vibrations) and lies between 1318 cm^{-1} and 1334 cm^{-1}. Lower frequencies indicate stronger hydrogen bonds with the substituent groups of the cation as can be seen, for example, in the crystal structure of **5** (Figure 2).

The attempted synthesis of 1-propargyl-3-methyl-imidazolium azide, **7**, did not result in an isolable product. One explanation might be reaction between the azide resin and the terminal alkyne group. It is well established that alkynes undergo a 1,3-cycloaddition with azides yielding 1,4-substituted 1,2,3-triazoles.[23] These types of reactions are also referred to as 'click chemistry'.[24] Intermediate triazoles could then undergo rapid thermal or photochemical reactions forming various products. A characterization of these possible products was not a subject of this investigation.

Physical properties. The melting, glass transition, and thermal decomposition temperatures determined by DSC are given in Table 1. Like their halide parents,[13] the IL azides showed a tendency to form supercooled liquids and might be easily mistaken for

true room-temperature ILs. Only after considerable time did some of the materials solidify, and could their melting points be accurately measured. Melting points range from 19°C for **6** up to 66°C for **5**. Nearly all the azides possess considerably lower melting points than the corresponding bromide salts. The most visible trend among the azides is a decrease in decomposition temperature going from saturated to unsaturated sidechains in the order of alkanes to alkenes to alkynes.

For ease of pumping and dispersal for combustion, it is desirable that propellants have low viscosities. Therefore, the viscosities of the room-temperature liquids or super-cooled liquids were measured (Table 1). They range between 201 to 4124 cP, not unexpectedly large considering chain length and saturation of the pendant groups. Although some of the pure compounds are too viscous for propellant applications, it is expected that this might be remedied with suitable additives.

Another key feature is the heat of formation of the compounds. Theoretical performance can be estimated from calculated heats of formation. In general, a promising compound should possess a high positive heat of formation, hopefully without inducing thermal instability or shock sensitivity. Table 1 lists the calculated solid-phase heats of formation for the compounds investigated. The enthalpy of melting for the liquids was neglected. For **2** and **3** the gas-phase heats of formation for the separate ions were calculated by the G2 method[25] using Gaussian 98.[26] For the other cations, these values were derived from MP2/6-31G(d)//HF/6-31G(d) enthalpies[27] from GAMESS[28], experimental[29-31] or G2 heats of formation of the other reactants, and the homodesmic[32] reactions given in the supplemental material.

In all cases, the sum of the enthalpies of the ions was then corrected for the lattice enthalpy of a solid as estimated using the procedures described by Jenkins[33] with the individual crystal ion volumes approximated by the volumes enclosed by the 0.001 electron contour of the HF/6-31G(d) electron density in the isolated ion. The heats of combustion (Table 1) were then calculated according to equation 2.

$$C_aH_bN_cO_d(l \text{ or } s) + (a + b/4 - d/2)O_2(g) \longrightarrow a\ CO_2(g) + b/2\ H_2O(l) + c/2\ N2(g) \quad (2)$$
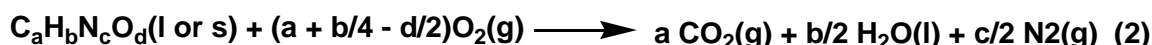
For easier comparison, data for known compounds, CH_3N_3,[34] $HOCH_2CH_2N_3$[34] and H_2NNH_2[35] are given as well.

Reactivity towards the common oxidizers IRFNA and N_2O_4. Most known energetic ILs consist of a heterocyclic cation and an oxygen-carrying anion,[36] and in bipropellant application, the cation would thus largely constitute the fuel. Consequently the positively charged fuel portion is rendered more resistant towards oxidation and this particular charge separation should lead to greater stability along with the other well known advantages of ILs (low vapor toxicity, consequent of low vapor pressure, etc.). However, this could also be a drawback for propulsion because of the greater expected resistance towards oxidation and resulting difficulty in achieving rapid (< 5ms) hypergolic ignition. Although oxidizer anions contribute to the overall performance (i.e., density and oxygen balance) they do not necessarily help with hypergolic ignition (as an extensively oxidized anion would not be expected to participate in oxidative pre-ignition reactions).

Consequently, in the present investigation, unsaturated hydrocarbon 'trigger groups' on the cation were combined with fuel-rich azide anions, in an effort to promote hypergolicity. Scheme 2 shows all tested IL azides. A typical experimental setup is shown in Figure 1. With IRFNA and N_2O_4, all compounds reacted vigorously with copious production of red fumes, but without ignition. [14]N NMR investigations of the residues revealed the formation of nitrates as suggested by equation (1). Volatile products were collected and examined using FTIR spectroscopy. With both oxidizers N_2O was observed, consistent with equation 1 and the fact that IRFNA contains significant quantities of N_2O_4 (IRFNA = 83% HNO_3 + 14% N_2O_4 + 1.5-2.5% H_2O + 0.6% HF). Treatment with IRFNA also led to observation of HN_3, produced by a displacement of the weaker acid from its salt.

The reaction of 1-methyl-4-amino-1,2,4-triazolium azide with N_2O_4 was additionally investigated under more gentle conditions than the drop tests. The solid residue was recrystallized from methanol layered with diethylether and identified as the new salt, 1-methyl-1,2,4-triazolium nitrate, **8**, by its Raman and NMR spectra and from single crystal X-ray investigation (Figure 3). This deaminated nitrate indicates that in these fuels both cation and anion participate in the oxidative reaction. It appears, however, that at these reaction conditions the initial heat release was not sufficient to further decompose the heterocyclic intermediates and yield hypergolic ignition, even when more reactive sidechains than a simple methyl group were built into the compound. The relatively large droplets may lack a sufficient surface-area-to-volume ratio and in this configuration (Figure 1) the oxidizer should be expected to serve as a heat sink. Nevertheless, under the same conditions, experiments carried out with hydrazine always led to rapid

hypergolic ignition. Because it is broadly accepted that ignition in known hypergolic systems takes place in the gas phase,[37] and one of the characteristics of ionic liquids is their low vapor pressure, further ignition experiments are underway to determine if finely dispersed droplets, in conditions more similar to existing engines, will ignite.

Crystal structure of 1-(2-butynyl)-3-methyl-imidazolium azide (5) and 1-methyl-1,2,4-triazolium nitrate (8). Single crystals of **5** were obtained from methanol layered with diethylether. **5** crystallized in the triclinic space group *P*-1 (Table 2). Figure 2 shows both the individual cation and anion and the hydrogen-bond network. The packing arrangement in the unit cell consists of two identical cation layers rotated by 180° and separated by azide anions. The pendant 2-butynyl group is bent slightly away from the imidazolium ring by 111.2° (N(2)-C(5)-C(6)), but lies almost in its plane, showing only a small dihedral twist of 17.4° (C(1)-N(2)-C(5)-C(6)). This twist is 10° larger than in the corresponding bromide salt,[13] attributable to hydrogen bonding with the azide anions. The azide anion shows four contacts (2.32Å to 2.45Å), which are more than 10% shorter than the sum of the Van der Waals radii (2.75Å) (Table 3).[38] Three of these contacts involve the CH_2-protons and one the H(1) ring proton. A longer hydrogen bond, 2.55Å is formed between N(5) of the azide anion and H(3) of the ring. In fact, these regions correspond to local maxima on the calculated electrostatic potential of the cation at the constant electron density contour as shown in the supplemental material. Three very weak contacts involve the methyl protons (2.68Å and 2.70Å) and the H(2) ring proton (2.63Å).

8 crystallized in an orthorhombic space group P_{nma} (Table 2). Figure 3 shows the individual cation and anion and the hydrogen-bond network. Note that H(3) has replaced the amino group which was attached to N(3) prior to the reaction with N_2O_4. The overall packing is dominated by attractive Coulomb forces accompanied by substantial hydrogen bonding from ring- and methyl-hydrogens to the nitrate anion. The packing arrangement consists of well-defined layers of alternating cations and anions. Within these layers, alternating cations are rotated by 90° and the view along the *a* axis demonstrates how the cations and anions are connected via hydrogen bonds. Figure 3 also shows that there are no contacts between the clearly separated layers. Hydrogen bonding dominates the structure and the shortest contacts are listed in Table 3. A remarkably strong hydrogen bond of only 1.79(3)Å connects the proton on the ring nitrogen to a nitrate oxygen (H(3)···O(2)). Indeed, the calculation for the isolated cation indicates that this region is highly electropositive (see supplemental material).

Conclusion. The series of known IL azides was expanded by synthesizing methylimidazolium heterocycles with saturated and unsaturated side-chains. Their reactivity toward common propellant oxidizers was investigated. In the case of the amino-triazolium salts, it was successfully demonstrated that both parts of the fuel, cation and anion, can react with the oxidizer. Unfortunately, the initial heat release during these reactions did not result in hypergolic ignition of the material under the tested conditions. The results are sufficiently encouraging to justify the expectation that variations in test conditions and ILs may lead to a practical IL hypergol.

Supporting Information Available. Crystallographic data for **5** and **8** in CIF format. The homodesmic reactions for the calculation of the gas-phase heats of formation of the cations of **1**, **4**, **5**, **6** and calculated electrostatic potential surfaces for the cations of **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Physicochemical properties of imidazolium azides and reference compounds.

	Imidazolium Cation	$T_{g(peak)}$ (°C)	$T_{m(peak)}$ (°C)	$T_{dec(onset)}$ (°C)	η/cP (25°C)	$\Delta_f H°$ (kcal mol^{-1})^c	$\Delta_c H°$ (kcal g^{-1})^c
1	1-butyl-3-methyl-	-74	+36	+222	404[a]	+73	-7.38
2	1-(hydroxyethyl)-3-methyl	-3	+36	+214		+40	-5.79
3	1-allyl-3-methyl-	-77	+19	+150	201	+107	-6.91
4	1-(3-butenyl)-3-methyl-	-57	+45	+188	495[a]	+101	-7.23
5	1-(2-butynyl)-3-methyl-		+66	+115		+143	-7.17
6	1-(2-pentynyl)-3-methyl-	-55	+19	+107	4124[b]	+139	-7.47
	H_2NNH_2[35]					+12	-4.64
	MeN_3[34]					+57	-4.45
	$HOCH_2CH_2N_3$[34]					+23	-4.39

[a] for super-cooled liquid; [b] 0.5 rpm; [c] estimated for solid phase

**Table 2** Crystal and structure refinement data for **5** and **8**.

Compound	1-(2-butynyl)-3-methyl-imidazolium azide (**5**)	1-methyl-1,2,4-triazolium nitrate (**8**)
Formula	$C_8H_{11}N_5$	$C_3H_6N_4O_3$
Space group	*P*-1 triclinic	*Pnma* orthorombic
a (Å)	7.195(1)	9.115(5)
b (Å)	8.238(2)	6.141(4)
c (Å)	8.447(2)	10.967(7)
α (°)	68.765(3)	90.000
β (°)	89.253(3)	90.000
γ (°)	80.307(3)	90.000
V/Å^3	459.4(2)	613.9(7)
$\rho_{calc.}$/g cm^{-3}	1.281	1.581
Z	2	4
Formula weight	177.22	146.12
μ/mm^{-1}	0.086	0.140
Temperature (K)	173(2)	173(2)
λ(MoKα)	0.71073	0.71073
Crystal size	0.30x0.20x0.10	0.60x0.10x0.10
Theta range θ/°	2.59 to 28.61	2.91 to 28.46
Index range	-9≤h≤9, -10≤k≤10, -10≤l≤11	-9≤h≤11, -4≤k≤8, -13≤l≤14
Reflection collected	5484	2475
Independent [R(int)]/	2164 [0.016]	768 [0.032]
Obs. refl. ([I > 2.0 σ(I)])	1980	704
F(000)	188	304
GooF	1.069	1.129
R$_1$, w*R* [I > 2σ(I)]	0.0449, 0.1131	0.0387, 0.0871
R$_1$, w*R*$_2$ (all data)	0.0487, 0.1156	0.0437, 0.1001
L.diff. peak/hole eÅ^3	0.25 and -.18	0.31 and -0.30
Absorption correct.	SADABS	SADABS
Data/restraints/param.	2164/0/162	768/0/78
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2

$R_1 = \Sigma \ ||F_o| - |F_c||/\Sigma|F_o|; \ R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{\frac{1}{2}}$

Table 3. Selected hydrogen contact lengths in Å of **5** and **8**.

salt	hydrogen contact	length
5	H(1)···N(3)	2.32(2)
	H(7)···N(5)	2.44(2)
	H(7)···N(4)	2.45(2)
	H(8)···N(3)	2.33(2)
8	H(3)···O(2)	1.79(3)
	H(3)···O(3)	2.54(3)
	H(1)···O(1)	2.39(3)
	H(1)···O(3)	2.51(2)
	H(2)···O(2)	2.19(3)
	H(4)···O(1)	2.51(3)

Scheme 1
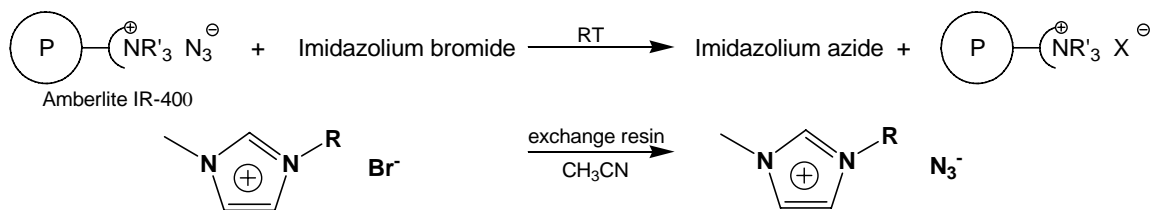
R = -butyl (**1**), -(2-hydroxyethyl) (**2**), -allyl (**3**), -(3-butenyl) (**4**), -(2-butynyl) (**5**), -(2-pentynyl) (**6**), -propargyl (**7**)
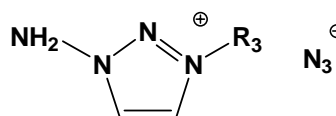
Scheme 2

1-methyl-imidazolium-based   4-amino-1,2,4-triazolium-based   1-amino-1,2,3-triazolium-based
IL azides

R_1 = -butyl, -allyl, -(3-butenyl), -(2-pentynyl); R_2 = -methyl, -allyl, -(2-hydroxyethyl), -(2-azidoethyl); R_3 = -allyl
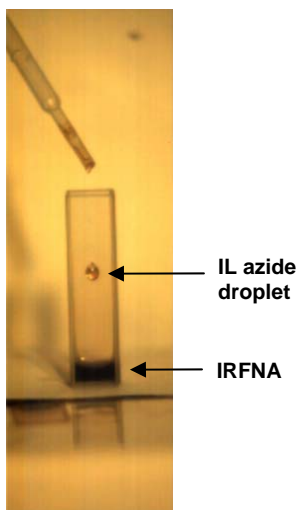
Figure 1.

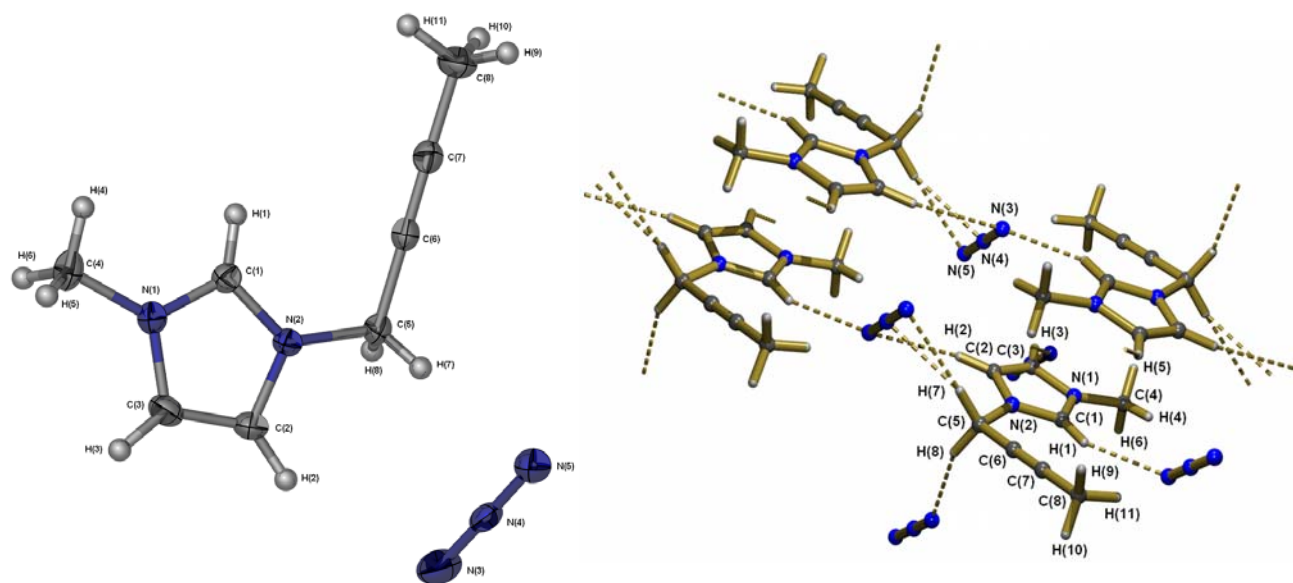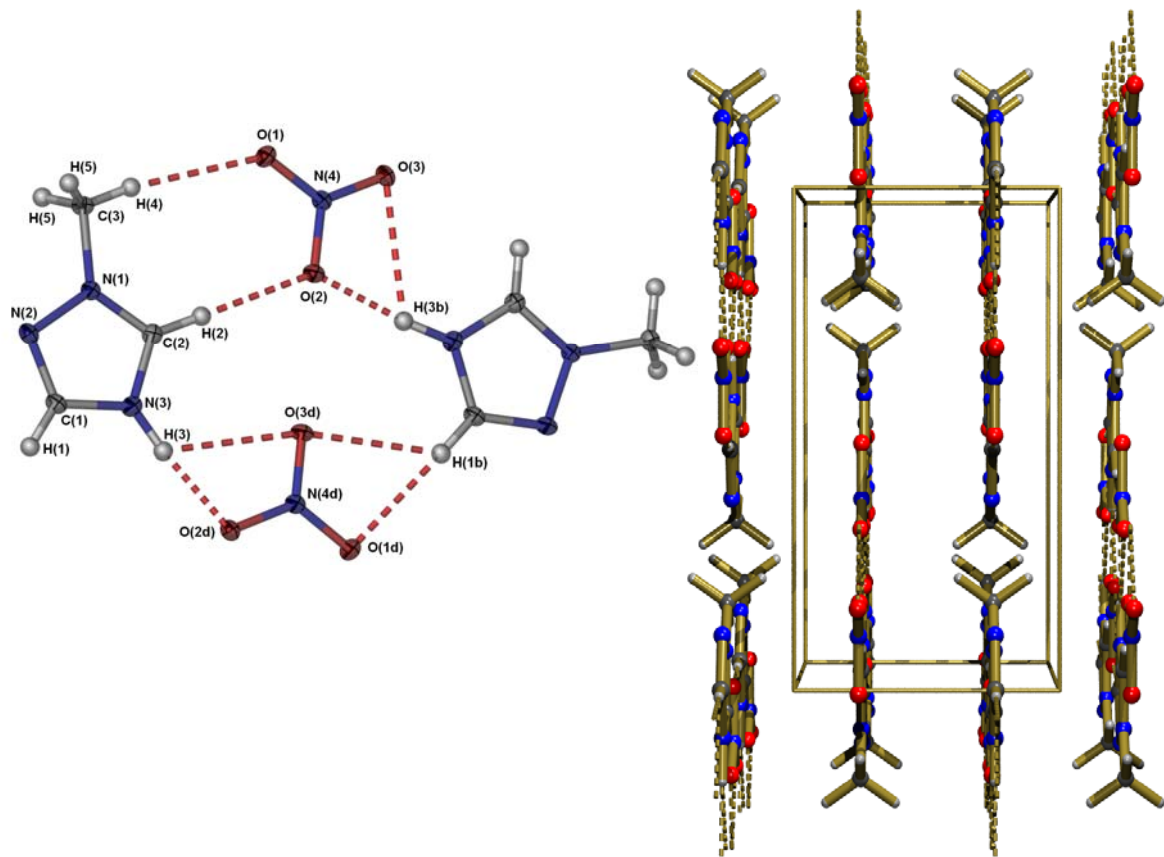

IL azide droplet

IRFNA

Figure 2.

Figure 3.

Figure 1. Shown is a typical experimental setup for a droplet experiment. The cuvette contains the oxidizer IRFNA or N_2O_4 to which an IL azide fuel droplet is added by means of a disposable pipette.

Figure 2. ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cation and anion present in the asymmetric unit and the hydrogen-bond network of 1-(2-butynyl)-3-methyl-imidazolium azide (**5**).

Figure 3. ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-methyl-1,2,4-triazolium nitrate (**8**) along the *a* axis.

Liquid azide salts and their reaction with common oxidizers

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Most of the toxicity problems associated with hydrazines relate to their high vapor pressures. Therefore, replacing hydrazines in bipropellant mixtures with an ionic liquid which generally possesses very low volatility, and therefore virtually no vapor toxicity, would be extremely beneficial. Consequently, the reactivity of previously and newly developed ionic liquid azides towards strong oxidizers like N_2O_4 and IRFNA were studied.

IL azide droplet

IRFNA

Hypergolic?